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L4	L3 and ethylene near8 (epoxy or glycidyl)	237	L4
L3	L2 and styrene	2276	L3
L2	polyamide elastomer or polyetheramide or polyamideether or polyesteretheramide or polyesteramide or polyetheresteramide or poly near2 (etheramide or amideether or esteretheramide or esteramide or etheresteramide)	6891	L2
L1	polyamide elastomer or polyetheramide or polyamideether or polyesteretheramide or polyesteramide or polyetheresteramide or poly near2 (etheramide or amideether or esteretheramide or yesteramide or etheresteramide)	6696	L1

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Aug 18, 1998

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TITLE: Resin composition for electrostatic coating - comprises rubber-reinforced styrene!-based resin, polyamide elastomer, denatured vinyl-based polymer having at least one functional group e.g. carboxyl, and an alkali metal salt

INVENTOR: AOKI, H; KAMIYAMA, S ; KOHAMA, K ; SAKANO, H ; TAKAGAWA, Y

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PATENT-FAMILY:

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JP 10219151 A	August 18, 1998		006	C09D005/44
EP 1148096 A1	October 24, 2001	E	000	C08L051/04
WO 9964512 A1	December 16, 1999	J	000	C08L051/04

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ABSTRACTED-PUB-NO: JP 10219151A

BASIC-ABSTRACT:

A resin composition consists of: (a) a 2-96.95 wt.% rubber-reinforced styrene-based resin; (b) a 96.95-2 wt.% polyamide elastomer; (c) a 1-50 wt.% denatured vinyl-based polymer having at least one functional gp. selected from a carboxyl gp., an epoxy gp., an amino gp., and an amide gp.; and (d) a 0.05-10 wt.% alkali metal salt.

Preferably the denatured vinyl-based polymer consists of a polymer of an ethylene-based unsaturated monomer having at least one functional gp. selected from a carboxyl, an epoxy, an amino, and an amide, and other ethylene-based unsaturated monomer.

USE - The resin composition is used in vehicular parts and finds its application in electrostatic coating.

ADVANTAGE - The resin composition has superior electrostatic coating without conductive primer treatment, and superior impact resistance.

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

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(54) 【発明の名称】 静電塗装用樹脂組成物

(57) 【要約】

【課題】 導電プライマー処理を施すことなく、静電塗装性に優れ、かつ耐衝撃性等の各種性能に優れた車両用部品等を提供しうる静電塗装用樹脂組成物を得ること。

【解決手段】 (A) ゴム強化スチレン系樹脂2～96.95重量%、(B) ポリアミドエラストマー96.95～2重量%、(C) カルボキシ基、エポキシ基、アミノ基、アミド基のうち少なくとも1種の官能基を有する変性ビニル系重合体1～50重量%および(D) アルカリ金属塩0.05～10重量%からなる静電塗装用樹脂組成物。

【特許請求の範囲】

【請求項1】 (A) ゴム強化スチレン系樹脂2～96.95重量%、(B) ポリアミドエラストマー96.95～2重量%、(C) カルボキシ基、エポキシ基、アミノ基、アミド基のうち少なくとも1種の官能基を有する変性ビニル系重合体1～50重量%および(D) アルカリ金属塩0.05～10重量%からなる静電塗装用樹脂組成物。

【請求項2】 変性ビニル系重合体(C)が、カルボキシ基、エポキシ基、アミノ基、アミド基のうち少なくとも1種の官能基を有するエチレン系不飽和単量体と他のエチレン系不飽和単量体との重合体である請求項1記載の静電塗装用樹脂組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、静電塗装用樹脂組成物に関する。詳しくは、導電プライマー処理を施すことなく、静電塗装性に優れた樹脂組成物に関するものである。

【0002】

【従来の技術】ゴム強化スチレン系樹脂は、塗装性、耐衝撃性、成形性に優れ、車両分野、電気製品、事務機器等の広範な分野に利用されている。中でも、車両分野への応用が多く、装飾ならびに耐候性改良のため塗装が行なわれる場合が多く見られる。しかしながら、成形品に塗装を実施した場合、塗料の塗着効率が悪くまた、複雑な形状を有する成形品において、塗装表面の品質が均一に保てないという問題があった。これらの問題を解決するための塗装方法として静電塗装が従来から行なわれている。しかしながらこの方法では、本来ゴム強化スチレン系樹脂が絶縁材料であるため、予め成形品表面に導電プライマー処理工程が必要である。また、導電カーボンを樹脂に配合する方法もとられているが、衝撃強度等の低下が大きい。

【0003】

【発明が解決しようとする課題】本発明は、上記問題点を解決すべく成されたもので、導電プライマー処理を施すことなく、静電塗装性に優れた樹脂組成物を提供することを目的とする。

【0004】

【問題点を解決するための手段】すなわち、本発明は、(A) ゴム強化スチレン系樹脂2～96.95重量%、(B) ポリアミドエラストマー96.95～2重量%、(C) カルボキシ基、エポキシ基、アミノ基、アミド基のうち少なくとも1種の官能基を有する変性ビニル系重合体1～50重量%および(D) アルカリ金属塩0.05～10重量%からなる静電塗装用樹脂組成物を提供するものである。

【0005】以下、本発明につき詳しく説明する。

【0006】ゴム強化スチレン系樹脂(A)とは、ゴム

状重合体(a-1)と芳香族ビニル系単量体、シアン化ビニル系単量体および/または不飽和カルボン酸アルキルエステル系単量体および共重合可能な他のビニル系単量体からなる単量体(a-2)とを重合してなる樹脂であり、上述のゴム状重合体(a-1)の存在下に単量体(a-2)を重合してなるグラフト重合体又は該グラフト重合体と単量体(a-2)を重合してなる共重合体との混合物である。

【0007】ゴム状重合体(a-1)としては、ポリブタジエン、スチレン-ブタジエン共重合体、アクリロニトリル-ブタジエン共重合体等のジエン系重合体、エチレン-プロピレン共重合体、エチレン-プロピレン-非共役ジエン系共重合体等のエチレン-プロピレン系共重合体、アクリル酸エステル系共重合体、塩素化ポリエチレン等が例示され、一種または二種以上用いることができる。

【0008】これらのゴム状重合体は乳化重合、溶液重合、懸濁重合、塊状重合等により製造される。なお、乳化重合により製造する場合におけるゴム状重合体のゲル含有率については特に制限はないが、0～95%であることが望ましい。

【0009】芳香族ビニル系単量体としてはスチレン、 α -メチルスチレン、 o -メチルスチレン、 m -メチルスチレン、 p -メチルスチレン、 t -ブチルスチレン、 α -メチルビニルトルエン、ジメチルスチレン、クロルスチレン、ジクロルスチレン、ブロムスチレン、ジブロムスチレン、ビニルナフタレン等が例示され、一種または二種以上用いることができる。特にスチレンが好ましい。

【0010】シアン化ビニル系単量体としては、アクリロニトリル、メタクリロニトリル、フマロニトリル等が例示され、一種または二種以上用いることができる。特にアクリロニトリルが好ましい。

【0011】不飽和カルボン酸アルキルエステル系単量体としては、メチル(メタ)アクリレート、エチル(メタ)アクリレート、プロピル(メタ)アクリレート、2-エチルヘキシル(メタ)アクリレート等が例示され、一種または二種以上用いることができる。特にメチルメタクリレートが好ましい。

【0012】上述の単量体と共にゴム強化スチレン系樹脂(A)を構成することのできる共重合可能な他のビニル系単量体としては、アクリル酸、メタクリル酸、マレイン酸、マレイン酸無水物、シトラコン酸無水物などの不飽和カルボン酸又は不飽和ジカルボン酸無水物、マレイミド、メチルマレイミド、エチルマレイミド、 N -フェニルマレイミド、 O -クロール- N -フェニルマレイミドなどのマレイミド化合物などがあげられ、それぞれ一種または二種以上用いることができる。

【0013】単量体(a-2)における芳香族ビニル系単量体(i)、シアン化ビニル系単量体および/または

不飽和カルボン酸アルキルエステル系単量体 (ii) および共重合可能な他のビニル系単量体 (iii) の組成比率には特に制限はないが、(i) 50~90重量%、(ii) 50~10重量%および (iii) 0~40重量%であることが好ましく、さらに好ましくは、(i) 50~80重量%、(ii) 50~20重量%および (iii) 0~30重量%であり、特に (ii) としてシアニ化ビニル系単量体を用いることが好ましい。

【0014】また、ゴム状重合体 (a-1) と単量体 (a-2) との組成比率にも特に制限はないが、ゴム状重合体 (a-1) 5~80重量%と単量体 (a-2) 95~20重量%であることが好ましい。

【0015】特にグラフト率20~100%および重量平均粒子径0.05~5 μ mのグラフト重合体と共重合体とからなる樹脂が好ましい。

【0016】ゴム強化スチレン系樹脂 (A) (グラフト重合体および共重合体) の製造方法にも特に制限はなく、公知の乳化重合、懸濁重合、塊状重合、溶液重合またはこれらを組み合わせた方法が用いられる。

【0017】ゴム強化スチレン系樹脂 (A) は、本発明樹脂組成物中に2~96.95重量%配合される。2重量%未満では、最終組成物の耐衝撃性、機械的強度が十分ではなくまた、流動性、外観、寸法安定性が悪い。一方96.95重量%を超すと、塗料塗着効率が改善されない。組成物の塗料塗着効率および剛性を含めた機械的特性の面より、5~50重量%が好ましい。

【0018】本発明におけるポリアミドエラストマー (B) とは、ハードセグメントとして炭素数が6以上のアミノカルボン酸またはラクタムもしくは $m+n \geq 12$ のナイロン m/n 塩 (X)、およびソフトセグメントとしてポリオール、例えばポリ (アルキレンオキシド) グリコール (Y) から構成され、かつエラストマー中の占める (X) 成分の比率が95~10重量%、好ましくは、90~20重量%のものである。エラストマー中に占める (X) 成分の比率が95重量%を越えると柔軟性に、10重量%未満であると耐薬品性に劣る傾向がある。

【0019】炭素数が6以上のアミノカルボン酸またはラクタムもしくは $m+n \geq 12$ のナイロン m/n 塩 (X) としては、 ω -アミノカプロン酸、 ω -アミノエナトン酸、 ω -アミノカプリル酸、 ω -アミノベルゴン酸、 ω -アミノカプリン酸、11-アミノウンデカン酸、12-アミノドデカン酸などのアミノカルボン酸あるいはカプロラクタム、ラウロラクタムなどのラクタムやナイロン6・6、6・10、6・12、11・6、11・10、11・12、12・6、12・10、12・12などのナイロン塩が挙げられる。

【0020】ポリ (アルキレンオキシド) グリコール (Y) としては、ポリエチレングリコール、ポリ (1, 2および1, 3プロピレンオキシド) グリコール、ポリ (テトラメチレンオキシド) グリコール、ポリ (ヘキサ

メチレンオキシド) グリコール、エチレンオキシドとプロピレンオキシドのブロックまたはランダム共重合体、エチレンオキシドとテトラヒドロフランのブロックまたはランダム共重合体などが挙げられる。これらの平均分子量は、500~3000である。

【0021】(X) 成分と (Y) 成分の結合は、エラストマー成分の末端基の応じてエステル結合またはアミド結合が考えられる。結合に応じてジカルボン酸やジアミンなどの第3成分を用いることができる。

【0022】ジカルボン酸としては、炭素数4~20のものであり、例えばテレフタル酸、イソフタル酸、フタル酸、ナフタレン-2, 6-ジカルボン酸、ナフタレン-2, 7-ジカルボン酸、ジフェニル-4, 4'-ジカルボン酸、ジフェノキシエタンジカルボン酸、3-スルホイソフタル酸ナトリウムのような芳香族ジカルボン酸、1, 4-シクロヘキサジカルボン酸、1, 2-シクロヘキサジカルボン酸、ジシクロヘキシル-4, 4'-ジカルボン酸のごとき脂環族ジカルボン酸および琥珀酸、シュウ酸、アジピン酸、ジカルボン酸が挙げられる。

【0023】ジアミンとしては、芳香族、脂環族、脂肪族ジアミン (ヘキサメチレンジアミン) などが挙げられる。

【0024】ポリアミドエラストマーは、ポリエーテルエステルアミドとも称されており、特開昭62-232450、特開昭63-33456、特開昭63-95251、特開平1-60647、特開平1-240553、特開平3-97751、特開平4-309547、特開平4-314741、特開平4-348150、特開平5-230365、特開平5-262971、特開平5-287161、特開平5-295191、特開平5-320497、特開平6-313079、特開平7-10989、特開平7-145368、特開平7-188475、特開平7-188476などに記載されるものが用いられる。

【0025】ポリアミドエラストマー (B) は、本発明樹脂組成物中に2~96.95重量%配合される。2重量%未満では、最終組成物の塗料塗着効率が改善されず、96.95重量%を超すと剛性が低下する。組成物の塗料塗着効率および剛性を含めた機械的特性の面より、5~50重量%が好ましい。

【0026】本発明における変性ビニル系重合体 (C) とは、1種または2種以上のビニル系単量体を重合して得られる構造を有し、分子鎖中にカルボキシル基、エポキシ基、アミノ基、アミド基のうち少なくとも1種の官能基を有する重合体である。このような変性ビニル系重合体 (C) の具体例としては、該官能基を有するエチレン系不飽和単量体を重合してなる重合体①、該官能基を有するエチレン系不飽和単量体と他のエチレン系不飽和単量体との重合体②、さらには他のエチレン系不飽和単量体を重合するに際し該官能基を有する重合開始剤およ

び/または連鎖移動剤を使用することにより重合体分子鎖中に官能基を導入してなる重合体③が挙げられるが、重合体中に占める官能基含有量の制御の容易さ、最終組成物の物性バランスの面より、重合体②が好ましい。

【0027】特に変性ビニル系重合体(C)の最も好ましい態様としては、カルボキシル基、エポキシ基、アミノ基、アミド基のうち少なくとも1種の官能基を有するエチレン系不飽和単量体0.1~50重量%および他のエチレン系不飽和単量体50~99.9重量%を重合してなる重合体である。

【0028】カルボキシル基を有するエチレン系不飽和単量体としては、アクリル酸、メタクリル酸、マレイン酸、無水マレイン酸およびイタコン酸等が、エポキシ基を有するエチレン系不飽和単量体としては、アクリル酸グリシジル、メタクリル酸グリシジルおよびイタコン酸グリシジル等が、アミノ基を有するエチレン系不飽和単量体としては、アクリル酸アミノエチル、メタクリル酸エチルアミノプロピル、メタクリル酸フェニルアミノエチルなどの(メタ)アクリル酸のアミノアルキルエステル誘導体、N-アセチルビニルアミンなどのビニルアミン誘導体、メタアリアルアミンなどのアリルアミン誘導体およびアミノスチレン等が、アミノ基を有するエチレン系不飽和単量体としては、アクリルアミド、N-メチルメタクリルアミド等がそれぞれ例示される。

【0029】他のエチレン系不飽和単量体としては、スチレン、 α -メチルスチレン、ビニルトルエン等の芳香族ビニル単量体、アクリロニトリル、メタクリロニトリル等のシアン化ビニル単量体、アクリル酸メチル、メタクリル酸メチル、アクリル酸エチル、メタクリル酸エチル等のエチレン系不飽和カルボン酸エステル単量体、マレイミド、N-フェニルマレイミド、N-シクロヘキシルマレイミド等のマレイミド単量体等が挙げられる。

【0030】官能基を有する重合開始剤の例としては、 γ 、 γ' -アゾビス(γ -シアノバレイン酸)および過酸化サクシン酸等のカルボキシル基を有する開始剤や、 α 、 α' -アゾビス(γ -アミノ- α 、 γ -ジバレロニトリル)およびp-アミノベンゾイルパーオキシド等のアミノ基を有する開始剤が挙げられ、また他の重合開始剤としては過硫酸カリウム、過酸化水素、過酸化ベンゾイル、過酸化ラウロイル等の過酸化物、アゾビスイソブチロニトリル等のアゾ化合物、クメンハイドロパーオキシド等の有機ハイドロパーオキシドと鉄塩等との酸化-還元系開始剤が挙げられる。また官能基を有する連鎖移動剤の例としては、メルカプトプロピオン酸、4-メルカプト安息香酸およびチオグリコール酸等のカルボキシル基を有する連鎖移動剤やメルカプトメチルアミン、N-(β -メルカプトエチル)-N-メチルアミン、ビス-(4-アミノフェニル)ジスルフィドおよびメルカプトアニリン等のアミノ基を有する連鎖移動剤が挙げられ、また他の連鎖移動剤としては、n-ドデシルメルカ

ブタン、n-ドデシルメルカブタン等のメルカブタン類、 α -メチルスチレンダイマー、タービノレン等が挙げられる。

【0031】また、変性ビニル系重合体(C)を重合する際の重合方法については、懸濁重合、塊状重合、乳化重合、溶液重合等いずれの方法によっても良く、特に限定されない。

【0032】変性ビニル系重合体(C)は、本発明樹脂組成物中に1~50重量%配合される。1重量%未満では耐水性および塗装膜密着性に劣り、また50重量%を超すと機械的強度、流動性、成形品の外観に劣り好ましくない。好ましくは3~20重量%である。

【0033】本発明のアルカリ金属塩(D)としては、塩化リチウム、臭化リチウム、ヨウ化リチウム、ヨウ化ナトリウム、ホウ水素化ナトリウム、ホウフッ化リチウム、ホウフッ化カリウム、テトラフェニルホウ酸リチウム、テトラフェニルホウ酸カリウム、テトラフェニルホウ酸ナトリウム、チオシアン酸リチウム、チオシアン酸ナトリウム、チオシアン酸カリウム、過塩素酸リチウム、過塩素酸ナトリウム、過塩素酸カリウム等の無機酸のアルカリ金属塩、トリフルオロ酢酸リチウム、トリフルオロ酢酸ナトリウム、トリフルオロ酢酸カリウム、トリフルオロメタンスルホン酸リチウム、トリフルオロメタンスルホン酸ナトリウム、トリフルオロメタンスルホン酸カリウム、酢酸リチウム、酢酸ナトリウム、酢酸カリウム、ドデシルベンゼンスルホン酸リチウム、ドデシルベンゼンスルホン酸カリウム、ドデシルベンゼンスルホン酸ナトリウム、ドデシルスルホン酸リチウム、ドデシルスルホン酸カリウム、ドデシルスルホン酸ナトリウム等の有機酸のアルカリ金属塩が挙げられ、一種または二種以上を併用してもよい。これらアルカリ金属塩の中で好ましくはドデシルベンゼンスルホン酸の様な核置換ベンゼンスルホン酸のアルカリ金属塩およびチオシアン酸カリウムである。

【0034】アルカリ金属塩(D)は、本発明樹脂組成物中に0.05~10重量%配合される。0.05重量%未満では塗料塗着効率に劣り、また10重量%を超すと熱安定性および成形品外観に劣るので好ましくない。好ましくは0.2~5重量%である。

【0035】本発明の樹脂組成物には、酸化防止剤〔例えば2,6-ジ-tert-ブチル-4-メチルフェノール、2-(1-メチルシクロヘキシル)-4,6-ジメチルフェノール、2,2-メチレンビス-(4-エチル-6-tert-メチルフェノール)、4,4'-チオビス-(6-tert-ブチル-3-メチルフェノール)、ジラウリルチオジプロピオネート、トリス(ジ-ノニルフェニル)ホスファイト、ワックス〕、紫外線吸収剤〔例えばp-tert-ブチルフェニルサリシレート、2,2'-ジヒドロキシ-4-メトキシベンゾフェノン、2-(2'-ヒドロキシ-4'-n-オクトキシフェニル)ベンゾト

リアゾール〕、滑剤〔例えばパラフィンワックス、ステアリン酸、硬化油、ステアロアミド、メチレンビスステアロアミド、エチレンビスステアロアミド、*n*-ブチルステアレート、ケトンワックス、オクチルアルコール、ラウリルアルコール、ヒドロキシステアリン酸トリグリセリド〕、難燃剤〔例えば、酸化アンチモン、水酸化アルミニウム、ほう酸亜鉛、トリクレジルホスフェート、トリス（ジクロロプロピル）ホスフェート、塩素化パラフィン、テトラプロモブタン、ヘキサプロモベンゼン、テトラプロモビスフェノールA〕、着色剤〔例えば酸化チタン、カーボンブラック〕、充填剤〔例えば炭酸カルシウム、クレー、シリカ、ガラス繊維、ガラス球、カーボン繊維〕、顔料等を必要に応じて添加することができる。

【0036】本発明の組成物には、更に、ポリカーボネート、ポリ塩化ビニル、ポリアミド、ポリブチレンテレフタレート、ポリエチレンテレフタレート、ポリフェニレンオキサイド、ポリオキシメチレン等の他の熱可塑性樹脂を必要に応じて混合することができる。

【0037】次に本発明を実施例に基づいて説明するが、本発明はかかる実施例のみに限定されるものではない。なお、配合組成における部および％は全て重量に基づくものである。

【0038】ゴム強化スチレン系樹脂（A）

A-1：ポリブタジエンラテックス（平均粒子径0.35μm、ゲル含有量80％）20部（固形分）、スチレン55部およびアクリロニトリル25部を公知の乳化重合法により重合した。得られた重合体ラテックスを塩析、脱水、乾燥処理し、A-1を得た。

【0039】ポリアミドエラストマー（B）

【0047】表面固有抵抗値

彫り込み寸法150mm×90mm×3mm厚の金型を用い、成形温度230℃で射出成形し、成形品を得た。試験片を23℃、55％相対湿度の条件で24時間状態調節した後、表面高抵抗計SM-10E（東亜電波工業（株）製）を用い、測定電圧500V、サンプリング時間10秒の条件にて表面固有抵抗値を測定した。

【0048】成形品外観

彫り込み寸法90mm×55mm×3mm厚の金型を用い、成形温度230℃で射出成形し、成形品を得た。得られた成形品の艶ムラの状態を目視にて判定した。○：良好～×：不良

【0049】塗料塗着重量および密着性

彫り込み寸法240mm×250mm×3.5mm厚の金型を用い、成形温度230℃で射出成形し、成形品を得た。得られた成形品につき、下記条件にて静電塗装を行った。

* B-1：ポリエーテルエステルアミド（三洋化成社製、ベレスタットIOS-6321）

B-2：ポリエーテルエステルアミド（東レ社製、ベパックス4011MA）

【0040】変性ビニル系重合体（C）

C-1：スチレン70部、アクリロニトリル27部およびアクリル酸3部を公知の乳化重合法により重合した。得られた重合体ラテックスを塩析、脱水、乾燥処理し、C-1を得た。

10 【0041】アルカリ金属塩（D）

D-1：ドデシルベンゼンスルホン酸ナトリウム

【0042】〔実施例1～3、比較例1～5〕上記各種成分を表1に示す組成にて混合し、1軸押出機にて溶融混練（220℃）、ペレットを得た。得られたペレットにつき、各物性試験片を成形した。なお、各物性は以下の方法にて測定した。また、測定結果を表1に示す。

【0043】耐衝撃性（ノッチ付アイゾット）

ASTM D-256に準拠（1/4インチ厚、23℃）。

20 【0044】流動性

ASTM D-1238に準拠（240℃、10kg）。

【0045】剛性

ASTM D-790に準拠。

【0046】成形収縮率

彫り込み寸法150mm×90mm×3mm厚の金型を用い、成形温度230℃で射出成形し、成形品を得た。成形後、室温で72時間放置した後、成形品の寸法をノギスを使用して0.01mmまで測定し、次式にて算出

*30 した。
金型寸法－成形品寸法

成形収縮率（％）＝ $\frac{\text{金型寸法}-\text{成形品寸法}}{\text{金型寸法}} \times 100$

金型寸法

※塗装機：レスプロ型回転式静電塗装機（ホンダエンジニアリング製 IVWベル型塗装機）

ベル直径 70φ

印可電圧 -60Kv

吐出量 100g/min

ガン距離 200mm

40 回転数 10000rpm

シェービングエア 0.4kg

CVスピード 5400mm/min

レスプロスピード 2600mm/min

塗料：2液硬化ウレタン塗料（日本油脂製 ハイウレタン#5000、#6500）

塗装条件：温度 27℃、湿度 65％RH

その後、80℃×2時間乾燥させた後、塗料塗着重量を測定した。また、上記静電塗装された成形品の密着性を以下の方法にて測定した。すなわち、片刃カミソリの切刃を塗面に対して約30度に保持し、素地に達する1m

※50

mの基盤目100個(10×10)を作成し、24mm幅のセロハン粘着テープを基盤目上に完全に密着させ、直ちにテープの一端を有効面に直角に保ち瞬間的に引き離し、剥離した個数/テスト数(100)にて表す。なお、塗装後の環境条件を変更し、次の2つの測定を行った。

*条件1;湿度95%、50℃×120時間放置後の密着性

条件2;湿度95%、50℃×240時間放置後の密着性

【0050】

* 【表1】

	実施例			比較例				
	1	2	3	1	2	3	4	5
— 組成 — (部)								
A-1	80	60	90	100	80	40	80	60
B-1	20	20	10	—	20	60	20	20
B-2	—	20	—	—	—	—	—	—
C-1	10	15	5	—	—	20	10	60
D-1	2	2	2	—	—	2	—	2
— 物性 —								
耐衝撃性 (kg・cm/cm)	30	38	25	20	23	42	32	18
流動性 (g/10mm)	40	63	32	25	43	68	38	29
剛性 (kg/cm ²)	1.7×10^4	1.3×10^4	2.2×10^4	2.4×10^4	1.7×10^4	0.8×10^4	1.7×10^4	1.8×10^4
成形収縮率 (%)	0.6	0.6	0.5	0.5	0.6	0.9	0.6	0.6
表面固有抵抗 (Ω)	2.0×10^8	8.0×10^8	1.0×10^{10}	$>10^{10}$	8.0×10^{12}	7.0×10^8	5.0×10^8	1.0×10^{10}
成形品外観	○	○	○	○	○	△	○	×
塗料塗着重量 (g)	1.03	1.08	0.84	0.17	0.55	1.12	1.01	0.82
密着性 条件1	100/100	100/100	100/100	100/100	3/100	65/100	100/100	100/100
条件2	100/100	100/100	100/100	100/100	0/100	23/100	100/100	100/100

【0051】

※つ耐衝撃性等の各種性能に優れるものであり、特に車両用部品として好適に使用できるものである。

【発明の効果】本発明の静電塗装用樹脂組成物は、導電プライマー処理を施すことなく、静電塗装性に優れ、か※30

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(54) **RESIN COMPOSITION FOR ELECTROSTATIC COATING**

(57) A resin composition for electrostatic coating, comprising a rubber-reinforced aromatic vinyl resin (A), a polyamide elastomer (B), a modified vinyl polymer (C) containing at least one functional group selected from among carboxyl, epoxy, amino and amido, and an alkali

metal salt (D); a formed resin article excellent in electrostatic coatability which is formed from the resin composition; and a formed resin article having electrostatic coating film which is produced by coating the articles electrostatically.

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Description**TECHNICAL FIELD**

5 **[0001]** The present invention relates to a resin composition for electrostatic coating, a resin article formed from the resin composition and a formed resin article produced by coating the resin article electrostatically.

BACKGROUND ART

10 **[0002]** Rubber-reinforced styrene resin is excellent in impact resistance, moldability and the like, and utilized in various fields including vehicle parts, electrical appliances, business equipment and so on.

[0003] Among these fields, the rubber-reinforced styrene resin is chiefly applied to the vehicle parts as being coated for improving design and weatherability.

15 **[0004]** However, in the case of coating an article formed from the rubber-reinforced styrene resin, there arise problems such as insufficiency in deposition efficiency of a coating composition and difficulty in maintaining uniformity of the quality of coating surface when the article has a complicated shape.

[0005] Electrostatic coating has heretofore been performed as a coating method for solving the above problems. However, the electrostatic coating necessitates a step of subjecting an article surface to a conductive primer treatment since the rubber-reinforced styrene resin inherently is an insulating material. A method of mixing a conductive carbon with the resin has also been employed; however, the method has a drawback that impact strength of a coating film is largely decreased.

DISCLOSURE OF INVENTION

25 **[0006]** The present invention was accomplished to solve the above problems. A main object of the invention is to provide a resin composition for electrostatic coating which comprises a rubber-reinforced aromatic vinyl resin such as a rubber-reinforced styrene resin and is useful for forming an article excellent in various physical properties such as impact resistance; the article formed from the resin composition being suitably used for forming thereon a satisfactory electrostatic coating film without a conductive primer treatment.

30 **[0007]** Another object of the invention is to provide a resin article formed from the resin composition comprising a rubber-reinforced aromatic vinyl resin, the resin article being excellent in electrostatic coatability and various physical properties.

[0008] The inventors carried out an extensive research considering the conventional techniques mentioned above, and found that it is possible to form a satisfactory electrostatic coating film, even without a conductive primer treatment, on a resin article formed from a resin composition comprising a specific rubber-reinforced aromatic vinyl resin, a polyamide elastomer, a modified vinyl polymer containing a specific functional group(s), and an alkali metal salt and that the formed article is excellent in various physical properties such as impact resistance, to thereby accomplish the present invention.

40 **[0009]** Thus, the present invention provides the following resin composition, resin article formed from the resin composition, and formed resin article produced by coating the article electrostatically.

1. A resin composition for electrostatic coating comprising a rubber-reinforced aromatic vinyl resin (A), a polyamide elastomer (B), a modified vinyl polymer (C) containing at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido, and an alkali metal salt (D).

45 2. The resin composition according to item 1, wherein the rubber-reinforced aromatic vinyl resin (A) is a graft copolymer obtainable by polymerizing monomer components (a-2) in the presence of a rubber-like polymer (a-1), or a mixture of said graft copolymer and a copolymer of the monomer components (a-2), the monomer components (a-2) comprising (i) an aromatic vinyl monomer, (ii) at least one monomer selected from the group consisting of a vinyl cyanide monomer and an alkylester monomer of unsaturated carboxylic acid and, when necessary, (iii) another copolymerizable vinyl monomer.

50 3. The resin composition according to item 1, wherein the polyamide elastomer (B) is obtainable by reacting polyol with at least one compound selected from the group consisting of aminocarboxylic acid having not less than 6 carbon atoms, lactam having not less than 6 carbon atoms and nylon mon salt ($m + n \geq 12$).

55 4. The resin composition according to item 1, wherein the modified vinyl polymer (C) is a copolymer of an ethylenically unsaturated monomer containing at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido with another ethylenically unsaturated monomer.

5. The resin composition according to item 1, wherein the alkali metal salt (D) is at least one compound selected from the group consisting of potassium thiocyanate and an alkali metal salt of dodecylbenzenesulfonic acid.

6. The resin composition according to any one of items 1-5, comprising 2-96.95 wt.% of the rubber-reinforced aromatic vinyl resin (A), 2-96.95 wt.% of the polyamide elastomer (B), 1-50 wt.% of the modified vinyl polymer (C) and 0.05-10 wt.% of the alkali metal salt (D) when a total amount of the rubber-reinforced aromatic vinyl resin (A), the polyamide elastomer (B), the modified vinyl polymer (C) and the alkali metal salt (D) is 100 wt.%.

7. A formed resin article excellent in electrostatic coatability, which is formed from the resin composition according to any one of items 1-6.

8. A formed resin article having electrostatic coating film, which is produced by electrostatically coating the resin article according to item 7.

[0010] The resin composition for electrostatic coating of the present invention comprises a rubber-reinforced aromatic vinyl resin (A), a polyamide elastomer (B), a modified vinyl polymer (C) containing at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido, and an alkali metal salt (D).

[0011] Components comprised in the resin composition of the present invention are described below.

(A) Rubber-reinforced aromatic vinyl resin

[0012] The rubber-reinforced aromatic vinyl resin is also known as a rubber-reinforced styrene resin, and is obtainable by polymerizing a rubber-like polymer (a-1) with monomer components (a-2) consisting of (i) an aromatic vinyl monomer, (ii) at least one monomer selected from the group consisting of a vinyl cyanide monomer and an alkylester monomer of unsaturated carboxylic acid and, when necessary, (iii) another copolymerizable vinyl monomer. The rubber-reinforced aromatic vinyl resin may preferably be a graft copolymer obtainable by polymerizing the monomer components (a-2) in the presence of the rubber-like polymer (a-1), or a mixture of the graft copolymer and a copolymer obtainable by polymerizing the monomer components (a-2).

[0013] Components constituting the rubber-reinforced aromatic vinyl resin are described below.

(a-1) Rubber-like polymer

[0014] Examples of the rubber-like polymer (a-1) includes polybutadiene, a styrene-butadiene copolymer, a acrylonitrile-butadiene copolymer and like diene polymers, an ethylene-propylene copolymer, an ethylene-propylene-unconjugated diene copolymer and like ethylene-propylene copolymers, acrylic ester copolymers, chlorinated polyethylene and the like. These rubber-like polymers (a-1) are used solely or in combination of two or more.

[0015] Preparation process of the rubber-like polymer is not limited, and the rubber-like polymer may be prepared by emulsion polymerization, solution polymerization, suspension polymerization, bulk polymerization or the like according to known conditions. A gel content of the rubber-like polymer is not limited, but may preferably be 0-95 %. It is particularly preferred to prepare the rubber-like polymer by the emulsion polymerization from the viewpoint of controllability of the gel content.

(a-2) Monomer components

[0016] The monomer components (a-2) comprise (i) an aromatic vinyl monomer, (ii) at least one monomer selected from the group consisting of a vinyl cyanide monomer and an alkylester monomer of unsaturated carboxylic acid and, when necessary, (iii) another copolymerizable vinyl monomer.

[0017] Examples of the aromatic vinyl monomer (i) includes styrene, α -methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, t-butylstyrene, α -methylvinyltoluene, dimethylstyrene, chlorostyrene, dichlorostyrene, bromostyrene, dibromostyrene, vinylnaphthalene and the like; among which styrene is particularly preferred. The aromatic vinyl monomer may be used solely or in combination of two or more.

[0018] The vinyl cyanide monomer and the alkylester monomer of unsaturated carboxylic acid (monomer (ii)) are used solely or in combination.

[0019] Examples of the vinyl cyanide monomer include acrylonitrile, methacrylonitrile, fumaronitrile and the like; among which acrylonitrile is particularly preferred.

[0020] Examples of the alkylester monomer of unsaturated carboxylic acid include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and the like; among which methyl methacrylate is particularly preferred.

[0021] These monomers may be used solely or in combination of two or more.

[0022] In the present invention, it is particularly preferred to use the cyanide vinyl monomer as the monomer (ii).

[0023] As another copolymerizable vinyl monomer (iii), a monomer copolymerizable with (i) the aromatic vinyl monomer and (ii) at least one monomer selected from the group consisting of the vinyl cyanide monomer and the alkylester monomer of unsaturated carboxylic acid may suitably be used, and, preferably, said another copolymerizable vinyl

monomer (iii) is also copolymerizable with the rubber-like polymer.

[0024] Specific examples of said another copolymerizable vinyl monomer include acrylic acid, methacrylic acid, maleic acid and like unsaturated carboxylic acids; maleic anhydride, citraconic anhydride and like anhydrides of unsaturated dicarboxylic acid; maleimide, methylmaleimide, ethylmaleimide, N-phenylmaleimide, O-chloro-N-phenylmaleimide and like maleimide compounds and the like. Said another copolymerizable vinyl monomer may be used solely or in combination of two or more.

(iv) Composition ratio of monomer components (a-2)

[0025] Proportions of the aromatic vinyl monomer (monomer (i)), at least one monomer (monomer (ii)) selected from the group consisting of a vinyl cyanide monomer and an alkylester monomer of unsaturated carboxylic acid, and another copolymerizable vinyl monomer (monomer (iii)) to be comprised in the monomer components (a-2) are not limited, but the monomer components (a-2) may preferably comprise, when a total amount of monomers (i), (ii) and (iii) is 100 wt. %, 50-90 wt.% of the monomer (i), 50-10 wt.% of the monomer (ii) and 0-40 wt.% of the monomer (iii), more preferably 50-80 wt.% of the monomer (i), 50-20 wt.% of the monomer (ii) and 0-30 wt.% of the monomer (iii).

Preparation of rubber-reinforced aromatic vinyl resin (A)

[0026] Preparation process of the rubber-reinforced aromatic vinyl resin (A) is not limited, but preferable is a process wherein a graft copolymer is prepared by polymerizing the monomer components (a-2) in the presence of the rubber-like polymer (a-1). A known method such as emulsion polymerization, suspension polymerization, bulk polymerization and solution polymerization or a method combining them may be employed for the polymerization.

[0027] A graft ratio and a weight average particle diameter of the graft copolymer obtained by the above method are not limited, but the graft ratio may preferably be about 20-100 % and the weight average particle diameter may preferably be about 0.05-5 μm .

[0028] The rubber-reinforced aromatic vinyl resin (A) used in the invention may be the graft copolymer or a mixture of the graft copolymer and the copolymer of the monomer components (a-2).

[0029] The rubber-reinforced aromatic vinyl resin (A) may preferably comprise 100-10 wt.% of the graft copolymer and 0-90 wt.% of the copolymer of the monomer components (a-2) when a total amount of the graft copolymer and the copolymer of the monomer components (a-2) is 100 wt.%. If the proportion of the graft copolymer is less than 10 wt.%, the resulting composition will undesirably be deteriorated in impact resistance.

[0030] In the preparation process of the graft copolymer, a copolymer of the monomer components (a-2) is produced as a by-product. The proportion of the graft copolymer mentioned above includes the amount of the by-product copolymer of the monomer components (a-2). In the present specification, "proportion of the copolymer of the monomer components (a-2)" means the proportion of the copolymer of the monomer components (a-2) prepared separately from the graft copolymer. A method for polymerizing the monomer components (a-2) is not limited, and a known method such as emulsion polymerization, suspension polymerization, bulk polymerization and solution polymerization or a method combining them may be employed for the polymerization.

[0031] Proportions of the rubber-like polymer (a-1) and the monomer components (a-2) to be used for the preparation of the rubber-reinforced aromatic vinyl resin (A) are not limited, but it is preferable to use, when a total amount of the rubber-like polymer (a-1) and the monomer components (a-2) is 100 wt.%, 5-80 wt.% of the rubber-like polymer (a-1) and 95-20 wt.% of the monomer components (a-2), in particular, 5-60 wt.% of the rubber-like polymer (a-1) and 95-40 wt.% of the monomer components (a-2). Here, in the case of employing only a graft polymer, the above proportions are those of the rubber-like polymer (a-1) and the monomer components (a-2) in the graft polymer and, in the case of employing a mixture of the graft polymer and the copolymer, the above proportions are those of the rubber-like polymer (a-1) and the monomer components (a-2) in the mixture.

(B) Polyamide elastomer

[0032] The polyamide elastomer (B) is also known as a polyetherester amide, and is obtainable by reacting at least one component selected from the group consisting of aminocarboxylic acid having not less than 6 carbon atoms, lactam having not less than 6 carbon atoms and nylon mn salts ($m + n \geq 12$) as a hard segment (hereinafter sometimes referred to as "component (X)") with polyol as a soft segment (hereinafter sometimes referred to as "component (Y)").

[0033] Among the component (X), upper limit of the number of carbon atoms of the aminocarboxylic acid having not less than 6 carbon atoms may preferably be about 12; examples of such aminocarboxylic acid include ω -aminocaproic acid, ω -aminobenzoic acid, ω -aminocaprylic acid, ω -aminopelargonic acid, ω -aminocapric acid, 11-aminoundecanoic acid, 12-aminododecanoic acid and the like.

[0034] Upper limit of the number of carbon atoms of the lactam having not less than 6 carbon atoms may preferably

be about 12; specific examples of such lactam include caprolactam, lauro lactam and the like.

[0035] The nylon mn salts ($m + n \geq 12$) are the salts comprising equimolar amounts of dicarboxylic acid having not less than 6 carbon atoms, preferably 6-12 carbon atoms, and diamine having not less than 6 carbon atoms, preferably 6-12 carbon atoms; specific examples of such nylon mn salts include nylon 6-6 salt, nylon 6-10 salt, nylon 6-12 salt,

nylon 11-6 salt, nylon 11-10 salt, nylon 11-12 salt, nylon 12-6 salt, nylon 12-10 salt, nylon 12-12 salt and the like.
[0036] Poly(alkyleneoxide)glycol may be used as the polyol which is the component (Y). Specific examples of the polyol include, polyethyleneglycol, poly(1,2 and 1,3 propyleneoxide)glycol, poly(tetramethyleneoxide)glycol, poly(hexamethyleneoxide)glycol, a block or random copolymer of ethyleneoxide and propyleneoxide, a block or random copolymer of ethyleneoxide and tetrahydrofuran, and the like. Average molecular weight of each of the polyol may suitably be about 500-3000.

[0037] Preparation process of the polyamide elastomer (B) is not limited, and a known process may be employed in the present invention. The polyamide elastomer (B) is obtainable by, for example, a process wherein a polyamide prepolymer is formed by reacting component (X) with dicarboxylic acid to prepare polyamide prepolymer, and then the polyamide prepolymer is polymerized with polyol, which is the component (Y), under a high temperature and a reduced pressure, a process wherein a carboxylic acid-terminated polyamide elastomer is produced by charging a reaction vessel with the component (X), component (Y) and dicarboxylic acid simultaneously, followed by reacting them at a high temperature and under an increased pressure and then the polyamide elastomer is polymerized under a normal pressure or a reduced pressure, or the like.

[0038] Dicarboxylic acid used in the preparation of the polyamide elastomer (B) may preferably have 4-20 carbon atoms; examples of which include terephthalic acid, isophthalic acid, phthalic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-2,7-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, diphenoxyethanedicarboxylic acid, sodium 3-sulfoisophthalate and like aromatic dicarboxylic acids, 1,4-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, dicyclohexyl-4,4'-dicarboxylic acid and like alicyclic dicarboxylic acids, succinic acid, oxalic acid, adipic acid, dicarboxylic acid and the like.

[0039] Ratio of the component (X) and the component (Y) may be such that proportion of the component (X) based on a total amount of the component (X) and the component (Y) is about 95-10 wt.%, preferably about 90-20 wt.%. If the proportion of the component (X) is higher than 95 wt.%, the resulting resin composition will be deteriorated in flexibility. In turn, if the proportion is lower than 10 wt.%, the resulting resin composition is tend to be deteriorated in chemical resistance.

[0040] The polyamide elastomer to be used in the present invention may suitably have a weight average molecular weight of about 5,000-100,000.

[0041] Specific examples of the usable polyamide elastomer include those disclosed in Japanese Unexamined Patent Publications Nos. 232450/1987, 33456/1988, 95251/1988, 60647/1989, 240553/1989, 97751/1991, 309547/1992, 314741/1992, 348150/1992, 230365/1993, 262971/1993, 287161/1993, 295191/1993, 320497/1993, 313079/1994, 10989/1995, 145368/1995, 188475/1995, 188476/1995 and the like.

(C) Modified vinyl polymer

[0042] The modified vinyl polymer (C) to be used in the present invention comprises as a base skeleton a vinyl polymer obtainable by polymerizing at least one vinyl monomer, and contains in the vinyl polymer at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido. At least one of these functional groups must be present per molecule.

[0043] Specific examples of such modified vinyl polymer include (1) a polymer obtainable by polymerizing an ethylenically unsaturated monomer having a functional group(s), (2) a copolymer of an ethylenically unsaturated monomer having a functional group(s) and another ethylenically unsaturated monomer, (3) a polymer obtainable by polymerizing an ethylenically unsaturated monomer using an initiator having a functional group(s) and/or a chain transfer agent having a functional group(s) to introduce a functional group(s) to a molecular chain of the polymer.

[0044] Among the modified vinyl polymers to be used in the invention, specific examples of the ethylenically unsaturated monomer having a functional group(s) usable for the production of the polymer (1) or (2) are as follows.

[0045] Examples of the ethylenically unsaturated monomer having carboxyl include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid and the like. Examples of the ethylenically unsaturated monomer having epoxy include glycidyl acrylate, glycidyl methacrylate, glycidyl itaconate and the like. Examples of the ethylenically unsaturated monomer having amino include aminoethyl acrylate, ethylaminopropyl methacrylate, phenylaminoethyl methacrylate and like aminoalkylester derivatives of (meth)acrylic acid, N-acetylvinylamine and like vinylamine derivatives, methallylamine and like allylamine derivatives, aminostyrene and the like. Examples of the ethylenically unsaturated monomer having amido include acrylamide, N-methylmethacrylamide and the like.

[0046] Examples of said another ethylenically unsaturated monomer usable for the production of the polymer (2) include styrene, α -methylstyrene, vinyltoluene and like aromatic vinyl monomers, acrylonitrile, methacrylonitrile and

like vinyl cyanide monomers, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate and like ester monomers of ethylenically unsaturated carboxylic acid, maleimide, N-phenylmaleimide, N-cyclohexylmaleimide and like maleimide monomers and the like.

[0047] Examples of the initiator having a functional group(s) usable for the production of the polymer (3) include those having carboxyl such as γ , γ' -azobis(γ -cyanovaleic acid) and succinic acid peroxide, those having amino such as α , α' -azobis(γ -amino- α , γ -divaleronitrile), p-aminobenzoylperoxide, and the like. Examples of the chain transfer agent having a functional group(s) include those having carboxyl such as mercaptopropionic acid, 4-mercaptobenzoic acid and thloglycolic acid and those having amino such as mercaptomethylamine, N-(β -mercaptoethyl)-N-methylamine, bis-(4-aminophenyl)disulfide, mercaptoaniline, and like chain transfer agents.

[0048] Polymerization method for preparing the modified vinyl polymer (C) is not limited, and may be any one of suspension polymerization, bulk polymerization, emulsion polymerization, solution polymerization and the like.

[0049] Known initiators and chain transfer agents may be used for the production of the polymer (1) or (2). Examples of the initiators include a peroxide such as potassium persulfate, hydrogen peroxide, benzoyl peroxide and lauroyl peroxide, an azo compound such as azobisisobutyronitrile, and oxidation-reduction initiators comprising an iron salt and an organic hydroperoxide such as cumenehydroperoxide. Examples of the chain transfer agent include n-dodecylmercaptan, t-dodecylmercaptan and like mercaptanes, α -methylstyrene dimer, terpinolene and the like.

[0050] In the production of the polymer (2), proportions of the ethylenically unsaturated monomer having a functional group(s) and said another ethylenically unsaturated monomer may differ depending on types of monomers to be used; however, there may preferably be used, based on a total amount thereof, about 0.01-99 wt.% of the ethylenically unsaturated monomer having a functional group(s) and about 1-99.99 wt.% of said another ethylenically unsaturated monomer, more preferably about 0.05-80 wt.% of the ethylenically unsaturated monomer having a functional group(s) and about 20-99.95 wt.% of said another ethylenically unsaturated monomer, particularly preferably about 0.15-50 wt.% of the ethylenically unsaturated monomer having a functional group(s) and about 50-99.9 wt.% of said another ethylenically unsaturated monomer.

[0051] Further, in the production of the polymer (3), amounts of the initiator having a functional group(s) and the chain transfer agent having a functional group(s) used for the polymerization of the ethylenically unsaturated monomer are not limited, but there may typically be used, based on 100 parts by weight of the ethylenically unsaturated monomer, about 0.01-5 parts by weight of the initiator and about 0.01-10 parts by weight of the chain transfer agent. The initiator and the chain transfer agent each having a functional group(s) may be used together, while they may be used in such a manner that one of them has a functional group(s) and the other does not. The ethylenically unsaturated monomer to be used in the production process of the polymer (3) does not necessarily have a functional group; however, it is of course possible to use an ethylenically unsaturated monomer having a functional group(s).

[0052] It is preferred to use the polymer (2) in the present invention from the viewpoints of easiness of adjusting a content of the functional group comprised in the polymer and balance of physical properties of the resulting composition.

(D) Alkali metal salt

[0053] Examples of the alkali metal salt (D) include lithium chloride, lithium bromide, lithium iodide, sodium iodide, sodium borohydride, lithium borofluoride, potassium borofluoride, lithium tetraphenylborate, potassium tetraphenylborate, sodium tetraphenylborate, lithium thiocyanate, sodium thiocyanate, potassium thiocyanate, lithium perchlorate, sodium perchlorate, potassium perchlorate and like alkali metal salts of inorganic acid; lithium trifluoroacetate, sodium trifluoroacetate, potassium trifluoroacetate, lithium trifluoromethanesulfonate, sodium trifluoromethanesulfonate, potassium trifluoromethanesulfonate, lithium acetate, sodium acetate, potassium acetate, lithium dodecylbenzenesulfonate, potassium dodecylbenzenesulfonate, sodium dodecylbenzenesulfonate, lithium dodecylsulfonate, potassium dodecylsulfonate, sodium dodecylsulfonate and like alkali metal salts of organic acid and the like. These metal salts may be used solely or in combination of two or more.

[0054] Among these alkali metal salts, potassium thiocyanate and an alkali metal salt of a nuclear substitution product of benzenesulfonic acid such as dodecylbenzenesulfonic acid may preferably be used in the present invention.

Resin composition of the present invention and resin article formed therefrom

[0055] The resin composition of the invention comprises the rubber-reinforced aromatic vinyl resin (A), the polyamide elastomer (B), the modified vinyl polymer (C) having at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido and the alkali metal salt (D).

[0056] Form of the resin composition of the invention is not limited insofar as the resin composition comprises the above four components. For example, each of the components may be mixed in the form of a powder or the like, but they may typically be mixed and melted to give a resin composition in the form of pellets so as to be used for the production of resin articles.

[0057] Method of mixing the components and order of the components to be added are not limited, and the components may be mixed simultaneously or by a multistage mixing comprising plural steps such as a step of mixing two or three components and a step of mixing the rest of the components. A known mixing apparatus such as a kneader, Banbury mixer, roll or the like may be used for mixing the components. After the mixing process, the mixture is pelletized

by an ordinary pelletizer or the like to give a composition in the form of pellets.
[0058] Proportions of the components to be comprised in the resin composition of the present invention is not crucial, but the resin composition may preferably comprise about 2-96.95 wt.% of the rubber-reinforced aromatic vinyl resin (A), about 2-96.95 wt.% of the polyamide elastomer (B), about 1-50 wt.% of the modified vinyl polymer (C) and about 0.05-10 wt.% of the alkali metal salt (D) when a total amount of the four components (A)-(D) is 100 wt.%. The resin composition obtained by mixing the components (A)-(D) in the above ratio is good in fluidity and so on and excellent in moldability. Further, it is possible to form a satisfactory electrostatic coating on a article formed from the resin composition without applying a conductive primer. Moreover, the article is excellent in various physical properties such as impact resistance, mechanical strength and the like and good in dimensional stability, appearance and so on.

[0059] In the case where the proportion of the rubber-reinforced aromatic vinyl resin (A) is too low, the resulting composition will be deteriorated in fluidity, and an article formed therefrom will be insufficient in impact resistance and mechanical strength and further be deteriorated in appearance and dimensional stability. In turn, if the proportion is too high, deposition efficiency of coating composition cannot be improved.

[0060] In the case where the proportion of the polyamide elastomer (B) is too low, deposition efficiency of coating composition cannot be improved. In turn, if the proportion is too high, the article formed from the resulting composition will be deteriorated in rigidity.

[0061] In the case where the proportion of the modified vinyl polymer (C) is too low, the article formed from the resulting composition will be deteriorated in water resistance and adhesion of coating. In turn, if the proportion is too high, the resulting composition will be deteriorated in fluidity, and an article formed therefrom will be deteriorated in mechanical resistance and appearance.

[0062] In the case where the proportion of the alkali metal salt (D) is too low, deposition efficiency of coating composition cannot be improved. In turn, if the proportion is too high, an article formed from the resulting composition will be deteriorated in thermostability and appearance.

[0063] More preferably, the resin composition of the present invention may comprise about 50-90 wt.% of the rubber-reinforced aromatic vinyl resin (A), about 5-50 wt.% of the polyamide elastomer (B), about 3-20 wt.% of the modified vinyl polymer (C) and about 0.2-5 wt.% of the alkali metal salt (D), based on 100 wt.% of a total amount of the four components (A)-(D), from the viewpoints of being good not only in deposition efficiency of coating composition but also in mechanical properties such as rigidity.

[0064] To the resin composition of the present invention, it is possible to add, when so required, an antioxidant (for example, 2,6-di-*t*-butyl-4-methylphenol, 2-(1-methylcyclohexyl)-4,6-dimethylphenol, 2,2-methylene-bis-(4-ethyl-6-*t*-methylphenol), 4,4'-thiobis-(6-*t*-butyl-3-methylphenol), dilaurylthiodipropionate, tris(dinonylphenyl)phosphite, wax), an ultraviolet absorbent (for example, *p*-*t*-butylphenyl salicylate, 2,2'-dihydroxy-4-methoxybenzophenone, 2-(2'-hydroxy-4'-*n*-octoxyphenyl)benzotriazole), a lubricant (for example, paraffine wax, stearic acid, hardened oil, stearamide, methylenebisstearamide, ethylenbisstearamide, *n*-butyl stearate, ketone wax, octyl alcohol, lauryl alcohol, hydroxy-stearic acid triglyceride), a flame retarder (for example, antimonous oxide, aluminium hydroxide, zinc borate, tricresyl phosphate, tris(dichloropropyl)phosphate, chlorinated paraffine, tetrabromobutane, hexabromobenzene, tetrabromobisphenol A), a colorant (for example, titanium oxide, carbon black), a filler (for example, calcium carbonate, clay, silica, glass fiber, glass beads, carbon fiber), a pigment and the like.

[0065] Amounts of these additives are not limited, and may suitably be adjusted depending on the purposes of using them. A total amount of the additives to be used may typically be about 0.01-100 parts by weight, preferably about 0.01-50 parts by weight, based on 100 parts by weight of a total amount of the components (A)-(D).

[0066] Further, when so required, another thermoplastic resin such as polycarbonate, polyvinyl chloride, polyamide, polybutylene terephthalate, polyethylene terephthalate, polyphenylene oxide and polyoxymethylene may be mixed with the resin composition of the present invention.

[0067] Amounts of the thermoplastic resins are not limited, and they may suitably be adjusted depending on the purposes of using them. A total amount of the thermoplastic resins to be used may typically be about 1-100 parts by weight, preferably 1-50 parts by weight, based on 100 parts by weight of a total amount of the components (A)-(D).

[0068] When forming the resin composition of the present invention into a desired shape, a forming method may be selected from conventional methods depending on the type of the target article. For example, the resin composition in the form of pellets as mentioned above may suitably be formed by a known forming method such as injection molding, extrusion forming, compression molding, blow molding and the like at a melted resin temperature of about 200-280°C and at a mold temperature of about 30-100°C.

[0069] The article formed from the resin composition of the present invention is good in electrostatic coatability and, therefore, it is possible to form an electrostatic coating on the article by an ordinary method without conductive primer

treatment. The coating thus formed is uniform in its coating surface quality even when the article had a complicated shape and is good in adhesion.

EFFECT OF THE INVENTION

[0070] The resin composition of the present invention is good in fluidity and moldability, and it is possible to form a satisfactory electrostatic coating on the article formed from the resin composition without a conductive primer. The article is excellent in various physical properties such as impact resistance and mechanical strength, and good in dimensional stability, appearances and the like.

[0071] The resin article has various applications such as vehicle parts, electric appliances, business equipment, etc. and, in particular, is suitably used for the vehicle parts.

BEST MODE FOR CARRYING OUT THE INVENTION

[0072] The present invention will be illustrated in the following based on examples, but the invention is not limited to the examples. In addition, "parts" and "%" in the composition ratios are based on weights unless otherwise stated.

(Examples 1-3 and Comparative Examples 1-5)

[0073] Components used in the examples and comparative examples are as follows.

Rubber-reinforced aromatic vinyl resin (A)

A-1: 20 parts (solid content) of polybutadiene latex (average particle diameter: 0.35 μ m; gel content: 80 %), 55 parts of styrene and 25 parts of acrylonitrile are polymerized by a known emulsion polymerization method. Obtained polymer latex was subjected to a salting-out treatment, dehydration and drying to give A-1.

Polyamide elastomer (B)

B-1: polyetherester amide ("PELESTAT IOS-6321", a product of Sanyo Chemical Industries, Ltd.).

B-2: polyetherester amide ("PEBAX 4011MA", a product of Toray Industries, Inc.).

Modified vinyl polymer (C)

C-1: 70 parts of styrene, 27 parts of acrylonitrile and 3 parts of acrylic acid are polymerized by a known emulsion polymerization method. Obtained polymer latex was subjected to a salting-out treatment, dehydration and drying to give C-1.

Alkali metal salt (D)

D-1: sodium dodecylbenzenesulfonate.

[0074] Above components were mixed in the proportions shown in Table 1. Compositions thus obtained were melted and kneaded by a uniaxial extruder at a temperature of 220°C to give pellets. As to the pellets, physical properties were measured according to the following methods. The measurement methods are described below. Results of the measurements are shown in Table 1.

Impact resistance (notched Izot)

[0075] By a method according to ASTM D-256, a test piece having a thickness of 1/4 inch was prepared from each of the compositions at a temperature of 230°C, and a notched Izot impact value of the test piece was measured at a temperature of 23°C.

Fluidity

[0076] By a method according to ASTM D-1238, the fluidity was measured under the conditions of a melting temperature of 240°C and with a load of 10 kg.

Rigidity

[0077] By a method according to ASTM D-790, a test piece having a thickness of 1/4 inch was prepared from each of the compositions at a temperature of 230°C and a flexural modulus of the test piece was measured at a temperature of 23°C.

Molding shrinkage

[0078] An article was molded from each of the compositions by injection molding at a temperature of 230°C using a mold having an impression of 150 mm x 90 mm x 3 mm. After allowing the article to stand for 72 hours at a room temperature, size thereof was measured with the accuracy of second decimal places (in millimeters) by using calipers, and the molding shrinkage was calculated from the following expression:

$$\text{Molding shrinkage (\%)} =$$

$$(\text{mold dimension} - \text{size of article}) \times 100 / \text{mold dimension}.$$

Surface resistivity

[0079] An article was molded from each of the compositions by injection molding at a temperature of 230°C using a mold having an impression of 150 mm x 90 mm x 3 mm. After conditioning the test piece under the conditions of a temperature of 23°C and a relative humidity of 55 % for 24 hours, the surface resistivity of the test piece was measured by using a surface resistivity meter "SM-10E" (product of Toa Electronics Ltd.), under the conditions of a measuring voltage of 500 V and a sampling time of 10 seconds.

Appearance of article

[0080] An article was molded from each of the compositions by injection molding at a temperature of 230°C using a mold having an impression of 95 mm x 55 mm x 3 mm. The article was visually observed of its evenness of luster for evaluation of its appearance, and the evaluation is shown based on the following criteria:

A: good; to C: bad.

Weight and adhesion of coating

[0081] An article was molded from each of the compositions by injection molding at a temperature of 230°C using a mold having an impression of 240 mm x 250 mm x 3.5 mm. Electrostatic coating was applied on the article under the following conditions.

Coating device:

Reciprocating rotary electrostatic coating device (IVW bell-shaped coating device, product of Honda Engineering Co., Ltd.);
Bell diameter: 70 φ;
Applied voltage: -60 Kv;
Discharge rate: 100 g/min;
Distance between gun and molded article: 200 mm;
Revolution: 10000 rpm;
Shaving air: 0.4 kg;
CV speed: 5400 mm/min;
Reciprocating speed: 2600 mm/min.

Coating material:

Two-pack type curable urethane coating composition (HIGH URETHANE #5000 and # 6500, products of NOF Corporation).

Coating conditions:

Temperature of 27°C; humidity of 65 %RH.

[0082] After performing the electrostatic coating under the above conditions, the coated article was allowed to stand for 2 hours at a temperature of 80°C to be dried. Then, a weight of coating formed on the article was measured.

[0083] Further, adhesion of the coating formed on the article was measured by the following method.

[0084] First, the coating film was cross-cut to reach the body of the article in order to form 100 cells (10 x 10) of 1 mm square using a middling razor, the cutting edge thereof being retained at an angle of about 30 degree with respect to the coating film. Then, a cellophane adhesive tape having a width of 24 mm was brought into close contact with the

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cross-cut portion, and the tape was instantly peeled off while one end thereof was retained at right angle with respect to the surface of the article, to thereby examine the adhesion of coating. Results are expressed by number of cells peeled off/number of tested cells (100).

[0085] Adhesion of the coating was measured under the following conditions.

5 [0086] Condition 1: Adhesion was measured after allowing a coated article to stand for 120 hours at a humidity of 95 % and a temperature of 50°C.

[0087] Condition 2: Adhesion was measured after allowing a coated article to stand for 240 hours at a humidity of 95 % and a temperature of 50°C.

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	Example			Comparative Example				
	1	2	3	1	2	3	4	5
-Proportions- (parts)								
A-1	70	50	85	100	80	40	70	25
B-1	18	18	8	-	20	58	20	18
B-2	-	15	-	-	-	-	-	-
C-1	10	15	5	-	-	-	10	55
D-1	2	2	2	-	-	2	-	2
-Physical Properties-								
Impact Resistance (kg·cm/cm)	28	32	22	20	23	42	27	12
Fluidity (g/10 min)	36	61	28	25	43	68	35	17
Rigidity (kg/cm ²)	1.8x10 ⁴	1.4x10 ⁴	1.8x10 ⁴	2.4x10 ⁴	1.7x10 ⁴	0.9x10 ⁴	1.8x10 ⁴	2.1x10 ⁴
Molding Shrinkage(%)	0.6	0.9	0.6	0.5	0.6	1.1	0.7	0.6
Surface Resistivity (Ω)	2.0x10 ⁹	7.0x10 ⁶	1.0x10 ¹⁰	>10 ¹⁶	3.0x10 ¹²	7.0x10 ⁷	3.5x10 ¹¹	5.2x10 ⁹
Appearance	A	A	A	A	A	A	A	C
Weight of Coating (g)	1.02	1.09	0.85	0.17	0.55	1.12	0.52	0.82
Adhesion: Condition 1	100/100	100/100	100/100	100/100	3/100	0/100	100/100	100/100
Condition 2	100/100	100/100	100/100	100/100	0/100	0/100	100/100	100/100

Claims

1. A resin composition for electrostatic coating comprising a rubber-reinforced aromatic vinyl resin (A), a polyamide

elastomer (B), a modified vinyl polymer (C) containing at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido, and an alkali metal salt (D).

2. The resin composition according to claim 1, wherein the rubber-reinforced aromatic vinyl resin (A) is a graft copolymer obtainable by polymerizing monomer components (a-2) in the presence of a rubber-like polymer (a-1), or a mixture of said graft copolymer and a copolymer of the monomer components (a-2), the monomer components (a-2) comprising (i) an aromatic vinyl monomer, (ii) at least one monomer selected from the group consisting of a vinyl cyanide monomer and an alkylester monomer of unsaturated carboxylic acid and, when necessary, (iii) another copolymerizable vinyl monomer.
3. The resin composition according to claim 1, wherein the polyamide elastomer (B) is obtainable by reacting polyol with at least one compound selected from the group consisting of aminocarboxylic acid having not less than 6 carbon atoms, lactam having not less than 6 carbon atoms and nylon mn salt ($m + n \geq 12$).
4. The resin composition according to claim 1, wherein the modified vinyl polymer (C) is a copolymer of an ethylenically unsaturated monomer containing at least one functional group selected from the group consisting of carboxyl, epoxy, amino and amido with another ethylenically unsaturated monomer.
5. The resin composition according to claim 1, wherein the alkali metal salt (D) is at least one compound selected from the group consisting of potassium thiocyanate and an alkali metal salt of dodecylbenzenesulfonic acid.
6. The resin composition according to any one of claims 1-5, comprising 2-96.95 wt.% of the rubber-reinforced aromatic vinyl resin (A), 2-96.95 wt.% of the polyamide elastomer (B), 1-50 wt.% of the modified vinyl polymer (C) and 0.05-10 wt.% of the alkali metal salt (D) when a total amount of the rubber-reinforced aromatic vinyl resin (A), the polyamide elastomer (B), the modified vinyl polymer (C) and the alkali metal salt (D) is 100 wt.%.
7. A formed resin article excellent in electrostatic coatability, which is formed from the resin composition according to any one of claims 1-6.
8. A formed resin article having electrostatic coating film, which is produced by electrostatically coating the resin article according to claim 7.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02610

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ C08L51/04, 77/12, 25/12, C08K5/42		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁶ C08L1/00-101/10, C08K3/00-13/08		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 4-337344, A (Toray Industries, Inc.), 25 November, 1992 (25. 11. 92), Claims (Family: none)	1-8
Y	JP, 8-253640, A (Mitsui Toatsu Chemicals, Inc.), 1 October, 1996 (01. 10. 96), Claims ; Par. No. [0024] (Family: none)	1-8
Y	JP, 8-48768, A (Sanyo Chemical Industries, Ltd.), 20 February, 1996 (20. 02. 96), Claims ; Par. No. [0031] (Family: none)	1-8
Y	JP, 8-81645, A (Japan Synthetic Rubber Co., Ltd.), 26 March, 1996 (26. 03. 96), Claims (Family: none)	1-8
Y	JP, 9-279024, A (Sanyo Chemical Industries, Ltd.), 28 October, 1997 (28. 10. 97), Claims ; Par. No. [0001] (Family: none)	1-8
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date. "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 24 August, 1998 (24. 08. 98)		Date of mailing of the international search report 1 September, 1998 (01. 09. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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